

THE IMPORTANCE OF PARTICLE INDUCED X-RAY EMISSION (PIXE) ANALYSIS AND IMAGING TO THE SEARCH FOR LIFE ON THE OCEAN WORLDS.

D.F. Blake,¹ P. Sarrazin² and Kathleen Thompson²
¹Exobiology Branch, MS 239-4, NASA Ames Research Center, Moffett Field, CA 94035 (david.blake@nasa.gov), ²SETI Institute, Mountain View, CA 94043.

Introduction: Microbial life exploits microscale disequilibria at boundaries where valence, chemical potential, pH, eH, etc. vary on a length scale commensurate with the organisms themselves - tens to hundreds of micrometers. These disequilibria can exist within cracks or veins in rocks and ice, at inter- or intra-crystalline boundaries, at sediment/water or sediment/atmosphere interfaces, or within fluid inclusions trapped inside minerals. Detection of accumulations of the biogenic elements C,N,O,P,S at appropriate concentrations on or in a mineral substrate would constitute permissive evidence of extant life, but context is also required. Does the putative biosignature exist in a habitable environment? Under what conditions of P, T, and chemical potential was the host mineralogy formed?

In searching for evidence of life on Ocean Worlds, detection and/or quantification of the biogenic elements C, N, O, P, S, as well as the cations of the rock-forming minerals (Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe) and anions such as Cl, F⁻ are important in establishing permissive evidence for life and context. In both terrestrial laboratories and landed planetary missions, these measurements are typically made with X-ray Fluorescence (XRF) or Particle Induced X-ray Emission (PIXE). While either an X-ray tube source (XRF) or a radioisotope source such as ²⁴⁴Cm (XRF/PIXE) can be used for fluorescence, ²⁴⁴Cm (used in all of the Alpha-Particle X-ray Spectrometer (APXS) instruments to date [1-4]) is preferred because the γ -rays at 14 and 18 KeV fluoresce the mid-range elements Ca – Mo, and the α -particles at 5.8 MeV strongly fluoresce the lower atomic number elements including C, N and O. With such a source, a fluorescence analysis would yield the biogenic elements C, N, O, P, S, as well as the cations and anions important for providing contextual mineralogy or chemistry. By comparison, an X-ray tube source operating in the 30 KeV range is typically very efficient at fluorescing higher Z elements but much less so for lower Z elements.

For spaceflight XRF applications, the use of a radioisotope source eliminates the high cost, complexity, risk, power requirement, thermal and vibration sensitivity and mass of an X-ray tube and HVPS – but brings with it the risks and safety precautions associated with handling ionizing and cancer-causing substances. The specific requirements of a particular space mission will dictate which source type would be more appropriate.

Scaling sources to meet science requirements:

The fluorescent sources must be chosen and scaled to meet the science requirements of the application: Sufficient flux to meet detection limits for minor elements and accuracy/precision limits for major elements. Empirical measurements utilizing an XRF test fixture and modeling utilizing PyMCA [5], XMIMSIM [6] and GEANT4 [7] were used to determine source flux requirements for a variety of test cases. Fig. 1 shows a comparison of measured vs. modeled fluorescence of a NIST basalt standard with a 30 mCi ⁵⁵Fe source.

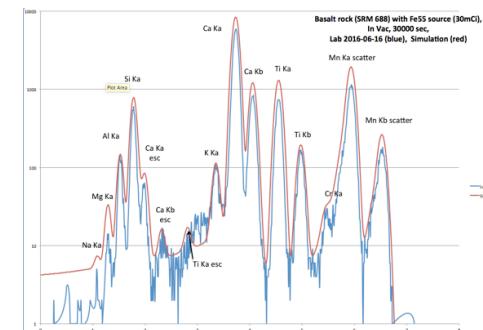


Fig. 1. XRF spectrum of NIST Basalt 688 obtained using a 30mCi ⁵⁵Fe γ -ray source measured in vacuum in an XRF test fixture (blue) vs. XMIMSIM simulation (red).

Figure 2 shows a comparison of modeled vs. measured fluorescence from a basalt sample using 30mCi ²⁴⁴Cm. Modeled α -particle excitation is shown in blue in fig. 2a, illustrating the strong fluorescence of low-Z elements afforded by PIXE.

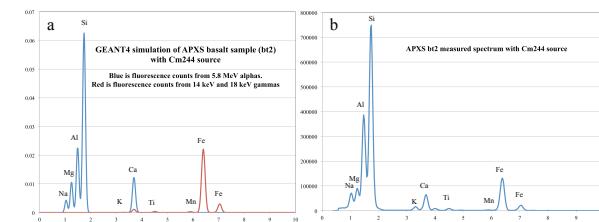


Fig. 2. Comparison of fluorescence from basalt sample bt2 using: (a) 30 mCi ²⁴⁴Cm source with 5.8 MeV α -particles (shown in blue), 14 and 18 KeV γ -rays (shown in red) modeled with GEANT4 vs. (b) published fluorescence data from the APXS instrument.

Calculation of k-values for detection and quantification of elements of interest: We used GEANT4 to model fluorescence of the biogenic elements and cations of the rock forming minerals with a 30 mCi ²⁴⁴Cm source. Calculations shown in Tables 1 and 2 assume integration over a sample area of 2 cm X 2 cm and an accumulation time of 10^4 sec (~3 hours). The

accumulation time for Table 3 was increased to 10^5 sec (~28 hours).

We calculate the significance level k as the number of counts in a characteristic peak divided by the square root of the background below the peak. $k > 2$ signifies successful detection at the 95% confidence level, $k > 10$ signifies successful quantification. Tables 1a and 1b show results for rock matrices and Tables 2-3 show results for ice matrices.

Element	Energy (KeV)	k-value (Basalt Matrix)	k-value (Silica Matrix)
P K α	2.02	1.9	1.9
S K α	2.31	3.8	4.2
Cl K α	2.62	3.0	4.2
K K α	3.31	3.5	3.9
Ti K α	4.51	1.4	3.9
Cr K α	5.41	2.3	5.6
Mn K α	5.90	1.7	8.4

Table 1a: Significance level k of K α peaks in two different rock matrices for trace element detection @ 100 ppm; $k > 2$ indicates detection at 95% confidence level. 30 mCi ^{244}Cm source, 10^4 sec run time.

Element	Energy (KeV)	k-value (Basalt Matrix)	k-value (Silica Matrix)
Na K α	1.04	140	170
Mg K α	1.25	140	260
Al K α	1.49	X	220
Si K α	1.74	X	X
Ca K α	3.69	240	210
Fe K α	6.40	X	560

Table 1b: Significance Level k of K α peaks in two different rock matrices for quantification of selected major elements, quantified to $1.0\% \pm 0.1$; $k > 10$ indicates successful quantification. (X=when an element is present in significant quantity in the matrix, k can't be calculated by this method.) 30 mCi ^{244}Cm source, 10^4 sec run time.

Element	Energy (KeV)	Weight %	k-value
C K α	0.282	0.1%	8.3
N K α	0.392	0.1%	18
Na K α	1.04	0.1%	23
Mg K α	1.25	0.1%	33
P K α	2.02	0.1%	80
S K α	2.31	0.1%	72
Cl K α	2.62	0.1%	57

Table 2. Significance level k for detection and quantification of biogenic and other low-Z elements present at 0.1% in a water ice matrix. 30 mCi ^{244}Cm source, 10^4 sec run time, $k > 10$ indicates successful quantification.

Element	Energy (KeV)	Concentration	k-value
C K α	0.282	1 microbe / 100X100 μm pixel	28
N K α	0.392	1 microbe / 100X100 μm pixel	11

Table 3. Significance level k for detection and quantification of C and N on a zero background filter through which melted Europa ice has been filtered. 1 microbe per 100X100 μm pixel over a 2 cm X 2 cm area. 30 mCi ^{244}Cm source, 10^5 sec run time, $k > 10$ indicates successful quantification.

Discussion: Monte Carlo simulations of ^{244}Cm (PIXE) fluorescence of the biogenic elements in rock and water ice matrices demonstrate the value of this technique to landed science on Ocean Worlds. Monte Carlo simulations of fluorescence using X-ray tube and/or radioisotope sources with γ -radiation only are shown to be inadequate for this application.

Historically, ^{244}Cm sources have only been manufactured in Russia, and an informal query of NASA centers indicates that a source of this type does not exist within the agency. To date, all quantitative elemental analyses on Mars since Viking have been obtained with ^{244}Cm sources, utilizing instruments contributed by other countries. We suggest that it is of strategic importance for NASA to develop such a source. Development will require the manufacture of a suitable curium compound (e.g., curium silicide), the development of an NRC-approved capsule having a thin foil cover to allow transmission of α -particles while blocking fission-induced sputtering of the material, testing the source and obtaining an NRC license for its use. Since the half-life of curium is 18 years, the sources can be manufactured and stored for long periods without loss of activity.

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